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(54) Title: FLUORINATED ALKENYLTRIAZINES AND THEIR USE AS CROSSLINKING AGENTS

(57) Abstract

Disclosed herein are novel fluorinated vinyl and allyl substituted fluoroalkyl containing triazines and a process in which they are used as curing agents for the crosslinking of suitable fluoroelastomers. These polymers are useful in elastomeric seals and for other uses in which high temperature and/or chemical resistance is needed.

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TITLE

FLUORINATED ALKENYLTRIAZINES AND THEIR USE AS CROSSLINKING AGENTS

FIELD OF THE INVENTION

This invention concerns selected novel fluorinated alkenyltriazines, and their use as crosslinking agents for fluorinated elastomers.

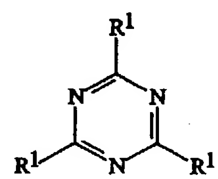
TECHNICAL BACKGROUND

Fluorinated elastomers are items of commerce, being used for a variety of applications where chemical and/or thermal resistance is important. They are especially useful for a variety of seals, such as O-rings and chevron rings. These elastomers are normally crosslinked when formed into their final part shapes, and it is desirable that the crosslinks formed have at least as much chemical and thermal stability as the elastomeric polymer itself.

One method of forming crosslinks with polymers which have certain functional groups attached is the free radical "grafting" of certain polyolefins, see for instance U.S. Patents 4,320,216, 4,303,761, 4,299,958 and 4,035,565, which are all hereby included by reference. The alkenyl triazines described herein give vulcanizates with good properties and have good curing characteristics, such as fast curing but good scorch resistance.

SUMMARY OF THE INVENTION

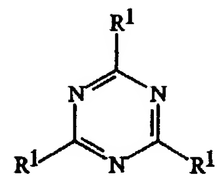
This invention concerns a compound of the formula



(I)

wherein R^1 is $CH_2{=}CH(CF_2)_n$-, $CH_2{=}CHCH_2(CF_2)_n$-, $CH_2{=}CHCF_2CF(CF_3)OCF_2CF_2$- or $CH_2{=}CHCF_2CF_2CF(CH{=}CH_2)OCF_2CF(CF_3)OCF_2CF_2$-, and n is an integer of 1 to about 10.

This invention also concerns a process for the crosslinking of a fluoro-elastomer, comprising, contacting a free radical generator, a fluoroelastomer which is capable of crosslinking with a polyolefin under free radical conditions, and a compound of the formula



(I)

wherein R^1 is $CH_2=CH(CF_2)_n$-, $CH_2=CHCH_2(CF_2)_n$-, $CH_2=CHCF_2CF(CF_3)OCF_2CF_2$- or $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2$-, and n is an integer of 1 to about 10, and provided said contacting is done at a temperature at which said free radical generator generates free radicals.

DETAILS OF THE INVENTION

By a fluoroelastomer herein is meant a polymer containing fluorine whose glass transition temperature and melting point (if any) is at or below about 40°C. It is preferred that the fluoroelastomer contain about 45% or more by weight of fluorine, and more preferred that it is a perfluoroelastomer.

Compound (I) can generally be made by the trimerization of a nitrile of the formula R^1CN (see Examples 9, 12, 15, 20 and 25). These nitriles, and precursors thereto, can be made by methods illustrated in the Examples or found in the following references: G. A. Grindahl, et al., J. Org. Chem., vol. 32, pp. 603-607 (1967); and P. B. Sargent, et al., J. Am. Chem. Soc., vol. 91, p. 415ff (1969).

In compound (I), when R^1 is $CH_2=CH(CF_2)_n$-, it is preferred that n is 1 or 2, when R^1 is $CH_2=CHCH_2(CF_2)_n$-, it is preferred that n is 1.

When (I) is used as a crosslinking agent, it may be used to crosslink fluororelastomers made from the following monomer combinations: hexafluoropropylene/vinylidene fluoride; tetrafluoroethylene/vinylidene fluoride/hexafluoropropylene; tetrafluoroethylene/perfluoro(alkyl vinyl ether) wherein the alkyl group contains 1 to 5 carbon atoms, preferably wherein the alkyl group is methyl or propyl; and tetrafluoroethylene/perfluoro(alkyl vinyl ether) wherein the alkyl group contains one or more ether oxygen atoms and 2 to 20 carbon atoms. In all of the these polymers, 0.1 to 5 mole percent (based on total repeat units) of a repeat unit derived from a curesite monomer may optionally be present. A curesite monomer is a monomer which provides a repeat unit which aids in the crosslinkng process. A crosslinked polymer wherein (I) is used as a crosslinking agent is also novel, since the crosslink itself has not been included in such polymers.

The crosslinked polymers of this invention are useful wherever chemical and/or high temperature resistance is required. They are especially useful in sealing

applications requiring such properties, such as in O-rings, chevron rings, gaskets, etc.

In the Examples, the following abbreviations are used:

Krytox® 16350 - poly(hexafluoropropylene oxide) available from E. I. du Pont de Nemours and Company, Wilmington, DE, USA

Luperco® 101XL - 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane

PCN42 - a postcure cycle under nitrogen of 6 h at 90°C, 10 h ramp from 90 to 304°C, and 26 h at 304°C

PCN260 - a postcure cycle under nitrogen of 8 h ramp to 260°C, and then 40 h at 260°C

TAIC - triallyl isocyanurate

In Examples 25-27, numbers such as DXXXX refer to ASTM test methods for the tests performed. Abbreviations used herein to give the test results are given in the ASTM test methods.

EXAMPLE 1

Preparation of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$

A 1 L autoclave was charged with 425 g of CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ and 335 g of hexafluoropropylene oxide and heated at 185°C for 10 hrs. The crude product (476.6 g) was distilled to give 391.6 g of pure product, bp 83-84°C/4.7 kPa. ^{19}F NMR: -80.4 (s, 3F), -83.5 (m, 2F), -85.2 to -86.4 (m, 2F), -121.6 (s, 2F), -145.7 (t, J = 22 Hz, 1F), -152.9 9d, J = 193.4 Hz, 2F), -155.7 (dm, J = 194 Hz, 2F), -162.4 (t, J = 8.7 Hz, 1F). ^1H NMR: 3.97 (s). IR(neat): 1791 (s), 1308 (s), 1276 (s), 1239 (s), 1152 (s). Anal: calcd for $C_{10}H_3F_{15}O_4$: C, 25.44; H, 0.64. Found: C, 26.19; H, 0.73.

EXAMPLE 2

Reaction of c-$C_3F_7OCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ with Iodine

A 1 L autoclave was charged with 200 g of c-$C_3F_7OCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ (c = cyclo) and 108 g of I_2 and heated at 150°C for 5 hr. The product was washed with aqueous Na_2SO_3 solution, checked by GC, indicating 90% of product with 10% of starting material, and distilled to give 236.5 g of pure $ICF_2CF_2CFIOCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$, bp 107-110°C/399 Pa, and 21.6 g of bp 60-106°C/399 Pa material containing starting material. ^{19}F NMR: -55.2 (d, J = 205.1 Hz, 1F), -58.8 (dm, J = 204.4 Hz, 1F), -69.0 (m, 1F), -80.0 (s, 3F), -79.6 to -80.7 (m, 1F), -82.5 to -84.0 (m, 2F), -89.9 (m, 0.5 F), -90.3 (m, 0.5F), -102.1 (d, J = 277.1 Hz, 1F), -104.6 (dt, J = 277 Hz, J = 8.4 Hz, 1F), -121.5 (s, 2F), -145.7 (t, J = 11.3 Hz, 0.5F), -146.0 (t, J = 11.7 Hz, 0.5F). ^1H NMR: IR(neat): 2990 (w), 1786 (s), 1306 (s), 1243 (s), 1194

(s), 1152 (s), 1134 (s0, 1128 (s). Anal: Calcd for $C_{10}H_3F_{15}I_2O_4$: C, 16.55: H, 0.42; I, 34.96. Found: C, 17.03; H, 0.51; I, 35.21.

EXAMPLE 3

Reaction of c-C_3F_5OCF2CF(CF_3)$OCF_2CF_2CO_2CH_3$ with Iodine at Higher Temperature

A 0.4 L shaker tube was charged with 189 g of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ and 100 g of I_2 and heated at 150°C for 3 hrs and 240°C for 8 hrs. Distillation of the reaction mixture gave 78.3 g of ICF_2CF_2COF, bp 57-58°C and 129.3 g of $ICF_2CF(CF_3)OCF_2CF_2CO_2Me$, bp 98-100°C/8.0 kPa. ^{19}F NMR for ICF_2CF_2COF: +28.0 (m, 1F), -62.1 (m, 2F), -111.4 (m, 2F); for $ICF_2CF(CF_3)OCF_2CF_2CO_2Me$: -58.8 (dm, J = 210 Hz, 1F), -59.9 (dm, J = 210 Hz, 1F), -76.8 (m, 3F), -82.7 (dm, J = 158.7 Hz, 1F), -83.7 (dm, J = 158 Hz, 1F), -121.6 (t, J = 3.3 Hz, 2F), -134.3 (m, 1F). IR for ICF_2CF_2COF: 1768 (s), 1187 (s), 1150 (s); IR for $ICF_2CF(CF_3)CF_2CF_2CO_2Me$: 1768 (s), 1342 9s), 1304 (s), 1232 to 1110 (s). Anal: Calcd. for $C_7H_3F_{10}IO_3$: C, 18.60; H, 0.67; F, 42.38; I, 28.08. Found: C, 18.24; H, 0.52; F, 42.38; I, 29.46.

EXAMPLE 4

Preparation of Ethyl 2-Iodotetrafluoropropanoate

A 300 mL shaker tube was charged with 50.8 g iodine and 50 g of trifluoromethoxylpentafluorocyclopropane and heated at 150°C for 4 hrs and 240°C for 8 hrs. After the tube was cooled to room temperature, 57.6 g of crude product was obtained, which was treated with 75 mL of EtOH and 11 g of KF at 10°C for 4 hours. The reaction mixture was poured into water. The lower layer was separated, washed with Na_2SO_3 solution and dried over molecular sieves to give 51.2 g of crude ester. Distillation gave 45.3 g of pure product, bp 72-73°C/4.0 kPa. ^1H NMR: 4.43 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H). ^{19}F NMR: -60.6 (t, J = 7.0 Hz, 2F), -111.9 (t, J = 7.0 Hz, 2F). IR (neat): 2995 (w), 1778 (s), 1374 (m), 1709 (s), 1185 (s), 1141 (s), 1076 (s). Anal: Calcd for $C_5H_5F_4IO_2$: C, 20.02; H, 1.68; F, 25.33; I, 42.30. Found: C, 19.83; H, 1.52; F, 27.74; I, 43.46.

EXAMPLE 5

Reaction of $ICF_2CF_2CO_2Et$ with Ethylene

A 0.4 L shaker tube was charged with 100 g of $ICF_2CF_2O_2Et$, 0.5 g of limonene and 20 g of ethylene and heated at 210°C for 6 hours. Distillation of the reaction mixture gave 85 g of pure product, bp 83-84°C/665 Pa and 11 g of 84% pure product, bp 35-84°C/665 Pa. ^{19}F NMR: -115.9 (t, J = 17.2 Hz, 2F), -120.4 (s, 2F). ^1H NMR: 4.41 (q, J = 7.1 Hz, 2H), 3.23 (m, 2H), 2.75 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H). IR (neat): 2995 (w), 1774 (s), 1320 (s), 1167 (s), 1134 (s), 1113

(s). Anal: Calcd for $C_7H_9F_4IO_2$: C, 25.63; H, 2.77; F, 23.17; I, 38.68. Found: C, 26.50; H, 2.86; F, 25.38; I, 39.38.

EXAMPLE 6

Preparation of $CH_2{=}CHCF_2CF_2CO_2Et$

To a stirred solution of 705.2 g of $ICH_2CH_2CF_2CF_2CO_2Et$ and 1 L of CH_2Cl_2 was slowly added 353 g of DBU over 3 hrs at 23 to 30°C. After the addition was complete, the reaction mixture was stirred at room temperature for 20 min. and then neutralized with 5% HCl solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and NaCl solution and dried over $MgSO_4$. After removal of CH_2Cl_2, the residue was distilled to give 331.5 g of $CH_2{=}CHCF_2CF_2CO_2Et$, bp 75°C/16 kPa.

EXAMPLE 7

Preparation of $CH_2{=}CHCF_2CF_2CONH_2$

To a stirred solution of 305 g (1.525 mol) of $CH_2{=}CHCF_2CF_2CO_2Et$ and 700 mL of CH_2Cl_2 was added 34 g (2.0 mol) of NH_3 at 0°C over 1.5 hrs. After the addition was complete, the resulting mixture was stirred at room temperature overnight. Removal of all volatiles gave 221.3 g of white solid product. ^{19}F NMR: -115.5 (2F), -122.0 (2F). ^1H NMR: 6.91 (br, 1H), 6.43 (br, 1H), 6.10-5.75 (m, 3H). IR(KBr): 3376 (m), 3268 (m), 3192 (m), 1706 (s), 1629 (m), 1245 (s), 1147 (s), 1014 (s), 956 (s).

EXAMPLE 8

Preparation of $CH_2{=}CHCF_2CF_2CN$

A mixture of 100 g of fine powder $CH_2{=}CHCF_2CF_2CONH_2$ and 261 g of P_2O_5 was heated at 130 to 170°C, during which volatiles were distilled out and collected in an ice-water cooled receiver. After 5 hours, 84.1 g of volatiles were obtained and GC analysis indicated the product was 97% pure. Two runs were combined, a drop of Hg added(to remove pink color), and distilled to give 160.7 g of colorless product, yield 90%, bp 53°C. ^{19}F NMR: -107.5 (t, J = 4.3 Hz, 2F), -11.4 (t, J = 4.3 Hz, 2F). ^1H NMR: 6.10 to 5.90 (m).

EXAMPLE 9

Trimerization of $CH_2{=}CHCF_2CF_2CN$

A 100 mL tube was charged with 40.0 g of $CH_2{=}CHCF_2CF_2CN$, 0.85 g of Ag_2O and cooled in liquid nitrogen. After being evacuated and pressured with nitrogen for six times, the tube was sealed and the contents in the tube were stirred at 120°C for 40 hours. The solids were dissolved in CH_2Cl_2 and transferred to a column with silica gel (CH_2Cl_2 as solvent) to give 35.0 g of pure $(CH_2{=}CHCF_2CF_2)_3C_3N_3$. ^{19}F NMR: -113.7 (d, J = 11.1 Hz, 6F), -118.1 (s, 6F).

IR: 1651 (w), 1552 (s), 1186-1014 (s). Anal: Calcd. for $C_{15}H_9F_{12}N_3$: C, 39.23; H, 1.98; N, 9.15. Found: C, 39.05; H, 1.94; N, 8.91.

EXAMPLE 10

Preparation of CH_2=$CHCF_2CF(CF_3)OCF_2CF_2CO_2Me$

A mixture of 68.0 g of $ICF_2CF(CF_3)OCF_2CF_2CO_2Me$ and 8.0 g of CH_2=CH_2 was heated in a 0.1 L shaker tube at 210°C for 6 hours, and 63 g of crude product was obtained. The crude product was diluted with 100 mL of CH_2Cl_2 and treated with 25 g of DBU at room temperature overnight. The reaction mixture was poured to water and neutralized with a 5% HCl solution. The lower layer was separated and washed with water. After removal of the CH_2Cl_2, the residue was distilled to give 40.1 g (76%) of CH_2=$CHCF_2CF(CF_3)OCF_2CF_2CO_2Me$, bp 71-72°C/2.7 kPa. ^{19}F NMR: -79.1 (m, 3F), -82.6 to -84.3 (m, 2F), -113.7 (dm J = 264.8 Hz, 1F), -115.0 (dm, J = 264.3 Hz, 1F), -121.9 (t, J = 3.0 Hz, 2F), -145.3 (t, J = 21.8 Hz, 1F). ^1H NMR: 3.96 (s, 3H), 5.99-5.78 (m, 3H).

EXAMPLE 11

Preparation of CH_2=$CHCF_2CF(CF_3)OCF_2CF_2CN$

A mixture of 21.1 g of CH_2=$CHCF_2CF(CF_3)OCF_2CF_2CO_2Me$ and 12.0 g of NH_4OH (30% in H_2O) in 25 mL of acetone was stirred at room temperature overnight. After removal of all volatiles, 17.3 g of crude CH_2=$CHCF_2CF(CF_3)OCF_2CF_2CONH_2$ was obtained. ^{19}F NMR: -79.1 (m, 3F), -82.5 (dd, J = 138.2 Hz, J = 24.0 Hz, 1F), -83.9 (dm, J = 138 Hz, 1F), -113.7 (dm, J = 264 Hz, 1F), -114.8 (dm, J = 264 Hz, 1F), -123.2 (m, 2F), -145.3 (m, 1F). ^1H NMR: 7.08 (br, 1H), 6.53 (br, 1H), 5.76-5.98 (m, 3H).

A flask fitted with a distillation head was charged with 13.0 g of the above amide and 18.0 g of P_2O_5 and was heated at 150 to 200°C for 2 hours, during which 9.3 g of CH_2=$CHCF_2CF(CF_3)OCF_2CF_2CN$ was collected in a receiver, bp 103 to 104°C, 97.5% purity. ^{19}F NMR: -79.1 (m, 3F), -83.6 (dm, J = 136 Hz, 1F), -85.3 (dm J = 136.8 Hz, 1F), -108.9 (m, 2F), -113.4 (dm, J = 264.8 Hz, 1F), -115.0 (dm, J = 265 Hz, 1F), -144.8 (m, 1F). ^1H NMR: 5.84 to 6.06 (m, 3H). Anal: Calcd for $C_8H_3F_{10}NO$: C, 30.11; H, 0.95; F, 59.54; N, 4.39. Found: C, 30.61; H, 1.17.

EXAMPLE 12

Trimerization of CH_2=$CHCF_2CF(CF_3)OCF_2CF_2CN$

A mixture was 4.0 g of CH_2=$CHCF_2CF(CF_3)OCF_2CF_2CN$ and 0.12 g of Ag_2O was stirred at 140 to 150°C for 15 hours and then purified by chromatography on silica gel using a mixture of hexane and ethyl acetate in a 90 to 10 ratio as eluent to give 3.5 g of pure $[CH_2$=$CHCF_2CF(CF_3)OCF_2CF_2]_3C_3N_3$.

^{19}F NMR: -79.4 (m, 9F), -82.30 (m, 6F), -113.8 (dm, J = 265 Hz, 3F), -114.6 (dm, J = 265 Hz, 3F), -119.4 (m, 6F), -144.8 (m, 3F). ^{1}HNMR: 5.98-5.75 (m, 9H). IR: 1651 (m), 1554 (s), 1423 (s), 1316 (s), 1219 to 1027 (s), 980 (s). Anal: Calcd for $C_{24}H_9F_{30}N_3O_3$: C, 30.11; H, 0.95; F, 59.54; N, 4.39. Found: C, 29.86; H, 1.02; F, 60.53; N, 4.45.

EXAMPLE 13

Preparation of $CH_2{=}CHCF_2CF_2CF(CH{=}CH)_2OCF_2CF(CF_3)OCF_2CF_2CO_2Me$

A mixture of 70.0 g of $ICF_2CF_2CFIOCF_2CF(CF_3)OCF_2CF_2CO_2Me$ and 12.0 g of $CH_2{=}CH_2$ was heated in a 0.1 L shaker tube at 160°C for 3 hours and 190°C for 2 hours, and 65 g of crude product was obtained. The crude product was diluted with 60 mL of CH_2Cl_2 and treated with 33.4 g of DBU at room temperature for 3 hours. The reaction mixture was poured to water and neutralized with a 5% HCl solution. The lower layer was separated and washed water. After removal of the CH_2Cl_2, the residue was distilled to give 28.3 g (58%) of $CH_2{=}CHCF_2CF_2CF(CH{=}CH_2)OCF_2CF(CF_3)OCF_2CF_2CO_2Me$, bp 108-110°C/665 Pa. ^{19}F NMR: -78.5 to -79.4 (m, 1F), -80.2 (m, 3F), -82.5 (m, 1F), -83.1 (dm, J = 138.5 Hz, 1F), -84.2 (dm, J = 138.5 Hz, 1F), -112.8 (s, 2F), -121.8 (m, 2F), -124.6 (dd, J = 282.7 Hz, J = 24.8 Hz, 1F), -125.3 (dm, J = 282.7 Hz, 1F), -127.8 (m, 1F), -145.8 (m, 1F). ^{1}H NMR: 3.95 (s, 3H), 5.10-5.69 (m, 6H). Anal: Calcd. for $C_{14}H_9F_{15}O_4$: C, 31.96; H, 1.72. Found: C, 31.98; H, 1.72.

EXAMPLE 14

Preparation of $CH_2{=}CHCF_2CF_2CF(CH{=}CH_2)OCF_2CF(CF_3)OCF_2CF_2CN$

A mixture of 20.0 g of $CH_2{=}CHCF_2CF_2CF(CH{=}CH_2)OCF_2CF(CF_3)OCF_2CF_2CO_2Me$ and 3.0 g of NH_3 in 40 mL of CH_2Cl_2 was stirred at room temperature for 20 hours. After removal of all volatiles, 19.0 g of crude $CH_2{=}CHCF_2CF_2CF(CH{=}CH_2)OCF_2CF(CF_3)OCF_2CF_2CONH_2$ was obtained. ^{1}H NMR: 8.11 (br, 1H), 7.80 (br, 1H), 6.34-5.84 (m, 6H).

A flask fitted with a distillation head was charged with 17.0 g of above amide and 18.0 g of P_2O_5 and was heated at 160 to 200°C for 2.5 hours, during which 14.7 g of $CH_2{=}CHCF_2CF_2CF(CH{=}CH_2)OCF_2CF(CF_3)OCF_2CF_2CN$ was collected in a receiver, bp 103 to 104°C. ^{19}F NMR: -78.1 to -79.0 (m, 1F), -80.3 (m, 3F), -81.6 to -82.4 (m, 1F), -84.3 (dm J = 134.8 Hz, 1F), -85.2 (dm J = 134.8 Hz, 1F), -108.8 (m, 2F), -112.8 (dm, 2F), -124.4 (ddd, J = 283.8 Hz, J = 28 Hz, J = 4 Hz, 1F), -125.6 (dd, J = 282.6 Hz, J = 10.0 Hz, 1F), -127.8.8 (m, 1F), -145.2 (m, 1F). ^{1}H NMR: 5.70-6.20 (m). Anal: Calcd. for $C_{13}H_6F_{15}NO_2$: C, 31.66; H, 1.23; N, 2.84. Found: C, 31.73; H, 1.40; N, 3.10.

EXAMPLE 15

Trimerization of CH_2=$CHCF_2CF_2CF(CH$=$CH_2)OCF_2CF(CF_3)OCF_2CF_2CN$

A mixture of 2.0 g CH_2=$CHCF_2CF_2CF(CH$=$CH_2)OCF_2CF(CF_3)OCF_2CF_2CN$ and 0.1 g of NH_3 was heated at 140°C in a sealed tube for 36 hours. The viscous oil was diluted with CH_2Cl_2 and transferred to a flask. After removal of solvent, the residue was purified by chromatography using ethyl acetate and hexane (9:1) as solvent to give 1.6 g of product. ^{19}F NMR: -78.3 to -78.9 (m, 3F), -80.5 (m, 9F), -81.9 to -83.3 (m, 3F), -113.1 (d, J = 7.3 Hz, 6F), -119.5 (m, 6F), -124.6 (dd, J = 283.6 Hz, J = 18.3 Hz, 3F), -126.0 (dd, J = 282.5 Hz, J = 18.2 Hz, 3F), -127.9 (m, 3F), -145.6 (m, 3F). IR: 3101 (w), 1735 (w), -1651 (w), 1555 (s), 1238-1008 (s). Anal: Calcd. for $C_{39}H_{18}F_{45}N_3O_6$: C, 31.66; H, 1.23; F, 57.78; N, 2.84. Found: C, 31.03; H, 1.45; N, 2.67.

EXAMPLE 16

Preparation of Ethyl 4-Iodo-2,2-difluorobutyrate

In a one-liter pressure reactor was charged ethyl iododifluoroacetate (200 g, 0.8 mol, from accompanied patent proposal), CH_3CN (80 mL) and water (300 mL). The mixture was cooled to -10°C and then a mixture of $Na_2S_2O_4$ (40 g) and $NaHCO_3$ (20 g) was added. The reactor was closed, cooled evacuated and charged with ethylene (60 g, 2.14 mol). The reaction mixture was then warmed to room temperature in a 4 hr period and kept at 40°C for 2 hr. After the reaction was over the lower layer was separated from the reaction mixture and the aqueous layer was extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. Distillation gave the title compound (200 g, 90% yield), bp. 70°C/266 Pa. ^{1}H NMR (300 MHz, $CDCl_3$): d1.38 (t, 3H), 2.70 (m, 2H), 3.20 (m, 2H), 4.37 (q, 2H). ^{19}F NMR (188.24 MHz, $CDCl_3$): -107.3 (t, J =16 Hz, 2F). Anal. Calcd. for $C_6H_9F_2IO_2$: C, 25.92; H, 3.26; F, 13.67. Found: C, 26.69; H, 3.28; F, 13.39. IR (neat): 1780 cm^{-1} (C=O). Mass: Calcd. for [$(M+H)^+$]: 278.9691; Found: 278.9659.

EXAMPLE 17

Preparation of Ethyl 2,2-Difluoro-3-butenoate

To a stirred solution of $ICH_2CH_2CF_2CO_2Et$ (450 g, 1.62 mol) in ether (1000 mL) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 260 g, 1.71 mol) in a 2 hr period. The temperature was maintained at between 10-20°C with external cooling. After the addition was complete, the reaction mixture was stirred at room temperature for 4 hrs. Water (600 mL) was added and the ethereal layer was separated and washed with brine, dried over $MgSO_4$. Distillation gave the desired product (200 g, 82% yield), bp. 60°C/9.3 kPa. ^{1}H NMR (300 MHz,

$CDCl_3$): d1.32 (t, 3H), 4.30 (q, 2H), 5.60 (d, 1H), 5.80 (dt, 1H), 6.00 (m, 1H). ^{19}F NMR (188.24 MHz, $CDCl_3$): -106.2 (2F). Anal. Calcd. for $C_6H_8F_2O_2$: C, 48.00; H, 5.37; F, 25.31. Found: C, 47.82; H, 5.72; F, 27.32. IR (neat): 1770 cm^{-1} (C=O), 1650 cm^{-1} (C=C). Mass: Calcd. for [$(M-CH_2=CH_2)^+$]: 122.0179; Found: 122.0191.

EXAMPLE 18

Preparation of 2,2-Difluoro-3-butenamide

Ethyl 2,2-difluoro-3-butenonate (51 g, 0.34 mol) was added dropwise into a solution of ammonium hydroxide (28-30 wt%, 24 g, 0.4 mol) and THF (25 mL) with stirring. The temperature was maintained at 10-20°C with external cooling during the addition. After addition was completed, the reaction mixture was stirred at ambient temperature for 3 hr. The disappearance of the starting material was monitored by GC. Extraction with ether followed by evaporation of solvent gave pure amide as a white crystal (30.5 g, 74%), mp. 85-86°C. ^1H NMR (300 MHz, acetone-d_6): d5.65 (m, 1H), 5.80 (m, 1H), 6.18 (m, 1H), 7.33 (br., 1H), 7.62 (br., 1H). ^{19}F NMR (188.24 MHz, acetone-d_6): -104.9 (2F). Anal. Calcd. for $C_4H_5F_2NO$: C, 39.68; H, 4.16; N, 11.57. Found: C, 39.83; H, 4.01; N, 11.23. IR (KBr): 3200, 3380 cm^{-1} (br, $CONH_2$), 1690 cm^{-1} (C=O), 1650 cm^{-1} (C=C). Mass: Calcd. for [$(M-F)^+$]: 102.0355; Found: 102.0372.

EXAMPLE 19

Preparation of 2,2-Difluoro-3-butenenitrile

2,2-Difluoro-3-butenamide (14.0 g, 0.118 mol) was well mixed with P_2O_5 (10 g) and heated slowly to 200°C. The product was distilled at 42-43°C to give the nitrile product (10.8 g, 91% yield). ^1H NMR (300 MHz, $CDCl_3$): d5.80 (m, 1H), 6.05 (m, 2H). ^{19}F NMR (188.24 MHz, $CDCl_3$): -86.5 (m, 2F). Mass: Calcd. for [M^+]: 103.0233; Found: 103.0227.

EXAMPLE 20

Preparation of 2,4,6-Tris(1',1'-difluoroallyl)-1,3,5-triazine

A mixture of 2,2-difluoro-3-butenenitrile (18.5 g, 0.18 mol) and ammonia (ca. 0.1 g) was heated at 120-130°C for 3 hr and then distilled to give the desired triazine product (17.8 g, 96% yield), bp.70°C/80 Pa. ^1H NMR (300 MHz, $CDCl_3$): d5.73 (d, 3H), 5.98 (d, 3H), 6.32 (m, 3H). ^{19}F NMR (188.24 MHz, $CDCl_3$): -103.6. IR (neat): 1554 cm^{-1} (triazine), 1650 cm^{-1} (C=C). Anal. Calcd. for $C_{12}H_9F_6N_3$: C, 46.61; H, 2.93; N, 13.59; F, 36.86. Found: C, 44.98; H, 3.13; N, 13.30; F, 38.08. Mass: Calcd. for [M^+]: 309.0700; Found: 309.0695.

EXAMPLE 21

Preparation of Ethyl 2,2-Difluoro-4-pentenoate

Ethyl iododifluoroacetate (100 g, 0.4 mol) was added dropwise into a well stirred suspension of copper powder (51 g, 0.803 mol) in anhydrous DMSO (250 mL) at room temperature. The temperature was maintained at below 25°C during the addition with external cooling. After that, the reaction mixture was stirred at room temperature for 45 min. Allyl bromide (60.5 g, 0.5 mol) was then added dropwise while the temperature was still controlled at 20-25°C during the addition. The reaction mixture was stirred at room temperature for another 3 hr after the addition was completed. Distillation in vacuo gave a crude product, which was extracted with ether, washed with brine and dried over $MgSO_4$. Redistillation produced pure ethyl 2,2-difluoro-4-pentenoate (52.8 g, 80% yield) as a clear, colorless liquid, bp. 55°C/2.7 kPa. ^{1}H NMR (300 MHz, $CDCl_3$): d1.25 (t, 3H), 2.76 (dt, 2H), 4.24 (q, 2H), 5.20 (1H), 5.22 (1H), 5.63 (m, 1H). ^{19}F NMR (188.24 MHz, $CDCl_3$): -105.7 (t, J = 18.9 Hz). IR (neat): 1780 cm^{-1} (C=O), 1650 cm^{-1} (C=C). Anal. Calcd. for $C_7H_{10}F_2O_2$: C, 51.22; H, 6.14; F, 23.15. Found: C, 49.73; H, 6.06; F, 21.42. Mass: Calcd. for [M$^+$]: 164.0648; Found: 164.0645.

EXAMPLE 22

Preparation of 2,2-Difluoro-4-pentenamide

To a stirred solution of ammonium hydroxide (28-30 wt%, 50 mL) and THF (200 mL) was added dropwise CH_2=$CHCH_2CF_2CO_2Et$ (51 g, 0.31 mol). The temperature was maintained at 20-25°C (external cooling if necessary) during the addition. The reaction was complete within 3 hr as monitored by GC. The product was worked up to give the corresponding amide compound (36 g, 86% yield), bp. 75°C/93 Pa.

^{1}H NMR (300 MHz, acetone-d_6): d2.85 (dt, J = 7.2 Hz, J =16 Hz, 2H), 5.20-5.30 (m, 2H), 5.70-5.85 (m, 1H), 7.25 (br., 1H), 7.58 (br., 1H). ^{19}F NMR (188.24 MHz, acetone-d_6): -105.3 (t, J =16 Hz, 2F). IR (neat): 3200-3500 cm^{-1} (N-H), 1720 cm^{-1} (C=O), 1650 cm^{-1} (C=C). Anal. Calcd. for $C_5H_7F_2NO$: C, 44.45; H, 5.22; N, 10.37; F, 28.12. Found: C, 42.31; H, 5.22; N, 10.18; F, 29.93. Mass: Calcd. for [M$^+$]: 135.0495; Found: 135.0490.

EXAMPLE 23

Preparation of 2,2-Difluoro-4-pentenenitrile

A mixture of CH_2=$CHCH_2CF_2CONH_2$ (33.8 g, 0.25 mol) and P_2O_5 (40 g) was heated slowly to 170-200°C to give the desired product as a colorless liquid (25.2 g, 86% yield), bp. 72-74°C. ^{1}H NMR (300 MHz, $CDCl_3$): d2.85 (dt, J = 7.2 Hz, J = 18 Hz, 2H), 5.30-5.50 (m, 2H), 5.62-5.78 (m, 1H). ^{19}F NMR

(188.24 MHz, $CDCl_3$): -89.5 (t, J =18 Hz). IR (gas): 2260 cm^{-1} (C≡N), 1650 cm^{-1} (C=C). Mass: Calcd. for [M^+]: 117.0390; Found: 117.0382.

EXAMPLE 24

Preparation of 2,4,6-Tris(1',1'-difluoro-3'-butenyl)-1,3,5-triazine

A mixture of 2,2-difluoro-4-pentenenitrile (23.4 g, 0.2 mol) and ammonia gas (ca. 0.1 g) was heated at 120°C for 10 hr in a sealed tube, and then distilled to give the desired triazine (18.5 g, 79% yield), bp. 86-90°C/93 Pa. ^{1}H NMR (300 MHz, $CDCl_3$): d3.15 (dt, J = 7.2 Hz, J = 16 Hz, 2H), 5.18-5.30 (m, 2H), 5.70-5.90 (m, 1H). ^{19}F NMR (188.24 MHz, $CDCl_3$): -103.1 (t, J =16 Hz, 2F). IR (neat): 1555 cm^{-1} (triazine), 1645 cm^{-1} (C=C). Anal. Calcd. for $C_{15}H_{15}F_6N_3$: C, 51.29; H, 4.30, N, 11.96; F, 32.45. Found: C, 50.50; H, 4.28; N, 11.80; F, 31.22. Mass: Calcd. for [M^+]: 351.1170; Found: 351.1164.

EXAMPLE 25

A perfluoroelastomer was prepared in a continuous polymerization process, similar to that described in U.S. Patent 4,983,697. The polymer was prepared in a 2 L mechanically stirred, water jacketed, stainless-steel autoclave operated continuously at 90°C and 6.2 MPa into which was pumped at a rate of 550 ml/h an aqueous polymerization medium/initiator solution comprising of 16 liters of water, 62 g of ammonium persulfate, 337 g of disodium hydrogen phosphate heptahydrate, 220 g of ammonium pefluorooctanoate ("Fluorad" FC-143 from 3M Co.). At the same time a separate solution of perfluoro(-(8-cyano-5-methyl-3,6-dioxa-1-octene) (8CNVE) was added at a rate of 7.4 g/h of 8CNVE. A gaseous stream of tetrafluoroethylene (113 g/h) and perfluoro(methyl vinyl ether) (PMVE, 130 g/h) were fed in the reactor at a constant rate by means of a diaphragm compressor. The polymer was continuously removed by means of a let-down valve and unreacted monomers were vented. The latex from 27.6 h of operation was combined and the polymer was coagulated by adding it with stirring to a hot (90-95°C) magnesium sulfate heptahydrate solution of about 3700 g in 80 L of water. The coagulated crumb was repeatedly washed with fresh water and dried at 80°C in an air oven. Analysis of the polymer by infrared indicated that the PMVE content was 44.6 wt%, TFE 53.1 wt% and 8CNVE 2.3 wt%. The inherent viscosity was 0.44 and the Mooney viscosity (ASTM D1646) was 32 as measured at 150°C and 86 as measured at 121°C.

The polymer was compounded on a rubber mill using the formulation shown in Table 1. The parts O-rings (size 214) and sheets were crosslinked by heating then in a hydraulic press at 175°C/30 min. under 3.45 MPa. They were then post-cured at 305°C for 42 hrs under nitrogen or at 225°C for 24 hr in air and tested using ASTM methods. Under column A we show the results of crosslinking

the above polymer using just peroxide and a coagent, using triallyl isocyanurate as the control and comparative results with the trivinyl perfluoroalkyl triazines where n = 2 (column B) and n = 1 (column C). The properties of parts molded as O-ring and as dumbbells are being compared.

TABLE 1

TRIS(VINYLTETRAFLUOROETHYLENE)TRIAZINE (TVTFET) AND TRIS(VINYLDIFULOROMETHYLENE)TRIAZINE (TVDFMT) AS COAGENTS IN THE PEROXIDE CURING OF PERFLUOROELASTOMER

	A (TAIC)	B (TVTFET)	C (TVDFMT)
COMPOUND			
Polymer	100	100	100
MT Black	30	30	30
Krytox® 16350	10	10	10
Luperco® 101XL	3	3	3
ZnO	2	2	2
TRIALLYL ISOCYANURATE	3	---	----
TVTFET	---	3	----
TVDFMT	---	---	3
ODR 177°/3° Arc D2084			
Ml, Nm	0.60	0.23	0.68
ts_2, mins	1.5	3.5	7.5
MH, Nm	2.5	1.7	1.8
MH-ML, Nm	1.9	1.5	1.1

PROPERTIES	O-Rings[1]	Dumb Bells[2]	O-Rings[1]	Dumb Bells[2]	O-Rings[1]
Tensile D1708					
M50, MPa	5.07		4.24		4.05
M100, MPa	9.04	8.36	8.50	8.87	7.11
Tb, MPa	12.1	14.7	13.6	17.7	8.94
Eb, %	144	260	173	230	143
Comp. Set 204°C/ 70 hr D1414	56		70		60

[1]Post-cured at 305°C/42 h under nitrogen (PCN42)

[2]Post-cured at 225°C/24 hr in air

EXAMPLE 26

The same polymer was used as described in Example 25. The formulation shown in Table 2 is based on the dual cure system which utilizes both the peroxide/coagent and the triphenyl tin hydroxide catalyst (TPT-OH).

TABLE 2

TRIS(VINYLTETRAFLUOROETHYLENE)TRIAZINE (TVTFET) AND TRIS(VINYLDIFULOROMETHYLENE)TRIAZINE (TVDFMT) AS COAGENTS IN THE DUAL CURE OF PERFLUOROELASTOMER

	A (TAIC)	B (TVTFET)	C (TVDFMT)
COMPOUND			
Polymer	100	100	100
MT Black	30	30	30
Krytox® 16350	10	10	10
ZnO	2	2	2
TPT-OH	1	1	1
Luperco® 101XL	1	1	1
TAIC	1	----	----
TVTFETriazine	----	1	----
TVDFMTriazine	----	----	3
ODR 177°/3° Arc D2084			
Ml, Nm	0.68	0.40	0.79
ts_2, mins	2.5	3.5	2.5
MH, Nm	4.6	3.2	3.1
MH-ML, Nm	4.0	2.8	2.3

PROPERTIES	O-Rings[1]	Dumb Bells[2]	O-Rings[1]	Dumb Bells[2]	O-Rings[1]
Tensile D1708					
M50, MPa	4.24		4.18	4.45	
M100, MPa	7.24	8.39	7.14	7.42	10.8
Tb, MPa	10.4	17.1	10.5	9.54	18.2
Eb, %	167	240	186	157	200
Comp. Set 204°C/ 70 hr D1414	54		58	60	

[1]Post-cured at 305°C/42 h under nitrogen (PCN42)

[2]Post-cured at 225°C/24 hr in air

EXAMPLE 29

Viton® GF (a copolymer of vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene and bromotrifluorobutene available from E. I. du Pont de Nemours and Company, Wilmington, DE, U.S.A.) was used in this Example. The formulation described in Table 3 was used.

TABLE 3

TRIS(VINYLTETRAFLUOROETHYLENE)TRIAZINE (TVTFET) AND TRIS(VINYLDIFULOROMETHYLENE)TRIAZINE (TVDFMT) AS COAGENTS IN THE PEROXIDE CURING OF VITON® GF

	A (TAIC)	B (TVTFET)	C (TVDFET)	D (TVDFMT)
COMPOUND				
Polymer	100	100	100	100
MT Black	30	30	30	30
MgO	3	3	3	3
Luperco® 101XL	3	3	3	3
TAIC	3	----	----	----
TVTFETriazine	----	3	1.5	----
TVDFMTriazine	----	----	----	1.5
ODR 177°/3° Arc D2084				
Ml, Nm	1.0	0.90	0.90	0.90
ts_2, mins	1.5	5.5	5.0	3.5
MH, Nm	4.3	2.4	2.6	2.4
MH-ML, Nm	3.3	1.5	1.7	1.5

PROPERTIES (O-Rings[1]) D1414				
M50, MPa	2.95	2.34		2.18
M100, MPa	8.06	4.83		4.43
Tb, MPa	14.6	14.1		11.7
Eb, %	143	215		202
Comp. Set 204°C/ 70 h D1414	53	73	79	58
(Dumbbells[2]) D1708				
M100, MPa	5.58	3.50	3.36	3.89
Tb, MPa	22.4	22.5	22.7	22.1
Eb, %	230	400	400	360

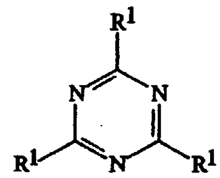
[1]Post-cured at 260°C/48 h under nitrogen (PCN260)

[2]Post-cured at 225°C/24 h in air

CLAIMS

What is claimed is:

1. A compound of the formula



(I)

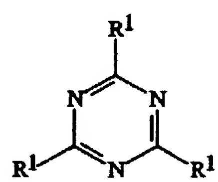
wherein R^1 is $CH_2=CH(CF_2)_n$-, $CH_2=CHCH_2(CF_2)_n$-, $CH_2=CHCF_2CF(CF_3)OCF_2CF_2$- or $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2$-, and n is an integer of 1 to about 10.

2. The compound as recited in Claim 1 wherein when R^1 is $CH_2=CH(CF_2)_n$- and n is 1 or 2.

3. The compound as recited in Claim 1 wherein R^1 is $CH_2=CHCH_2(CF_2)_n$- and n is 1.

4. The compound as recited in Claim 1 wherein R^1 is $CH_2=CHCF_2CF(CF_3)OCF_2CF_2$- or $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2$-.

5. A process for the crosslinking of a fluoroelastomer, comprising, contacting a free radical generator, a fluoroelastomer which is capable of crosslinking with a polyolefin under free radical conditions, and a compound of the formula



(I)

wherein R^1 is $CH_2=CH(CF_2)_n$-, $CH_2=CHCH_2(CF_2)_n$-, $CH_2=CHCF_2CF(CF_3)OCF_2CF_2$- or $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2$-, and n is an integer of 1 to about 10, and provided said contacting is done at a temperature at which said free radical generator generates free radicals.

6. The process as recited in Claim 5 wherein said fluoroelastomer is a copolymer of hexafluoropropylene/vinylidene fluoride; tetrafluoroethylene/vinylidene fluoride/hexafluoropropylene; tetrafluoroethylene/perfluoro(alkyl vinyl ether) wherein the alkyl group contains 1 to 5 carbon atoms, or and tetrafluoroethylene/perfluoro(alkyl vinyl ether) wherein the alkyl group contains one or more ether oxygen atoms and 2 to 20 carbon atoms.

7. The process as recited in Claim 5 wherein R^1 is $CH_2{=}CH(CF_2)_n$- and n is 1 or 2, or R^1 is $CH_2{=}CHCH_2(CF_2)_n$- and n is 1.

8. The product of the process of Claim 5.

9. The product of the process of Claim 6.

10. The process as recited in Claim 6 wherein said fluoroelastomer also contains 0.1 to 5 mole percent of a curesite monomer.

11. The product of the process of Claim 10.

12. The process as recited in Claim 5 wherein said fluoroelastomer contains 0.1 to 5 mole percent of a curesite monomer.

13. The process as recited in Claim 5 wherein said fluoroelastomer is a tetrafluoroethylene/perfluoro(alkyl vinyl ether) copolymer wherein the alkyl group is methyl or propyl.

14. The process as recited in Claim 13 wherein said fluoroelastomer contains 0.1 to 5 mole percent of a curesite monomer.

15. The product of the process of Claim 7.

16. The product of the process of claim 14.

INTERNATIONAL SEARCH REPORT

Interr. al Application No
PCT/US 96/12384

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D251/24 C08J3/24 C08K5/3492

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C08J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,3 847 916 (DOW CORNING CORPORATION) 12 November 1974 * complete document * ---	1-3,5
Y	US,A,3 532 696 (DOW CORNING CORPORATION) 6 October 1970 * complete document * ---	1-3,5
Y	US,A,3 810 874 (MINNESOTA MINING AND MANUFACTURING COMPANY) 14 May 1974 * example 6; complete document * ---	1-3,5
Y	US,A,3 654 273 (PCR,INC.) 4 April 1972 * complete document * --- -/--	1-3,5

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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2

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 1996	15. 10. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Van Bijlen, H

International Application No
PCT/US 96/12384

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 320 216 (E.I. DU PONT DE NEMOURS AND COMPANY) 16 March 1982 cited in the application see column 1-2 ---	1
A	US,A,4 035 565 (E.I. DU PONT DE NEMOURS AND COMPANY) 12 July 1977 cited in the application * complete document * -----	1

2

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 96/12384

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		DE-A-	1928050	11-12-69
		FR-A-	2014152	17-04-70
		NL-A-	6908387	05-12-69
		US-A-	3532696	06-10-70
US-A-3532696	06-10-70	BE-A-	733948	02-12-69
		DE-A-	1928050	11-12-69
		FR-A-	2014152	17-04-70
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		AU-A-	3317471	15-03-73
		AU-B-	469118	05-02-76
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